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STRUCTURE AND PHYSICAL PROPERTIES OF MOLTEN SALTS.

FINAL REPORT

~~December~~ 1, 1960 - ~~November~~ 30 1962,

by

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SUMMARY

Knowledge of the behavioral aspects (structure, physical properties) of pure one-component salts in the molten state is of fundamental importance for the problem of interactions and chemical bonding in molten salts quite generally. In this program the properties and structures of molten nitrates and mercuric halides have been characterized; the former are examples of highly ionic systems and the latter are predominantly molecular molten salts. Studies of molten salt-mixtures using the preceding both as solutes and solvents are in progress. An interesting result is that a molecular salt such as $HgCl_2$ can be readily "dissolved" in fused salt solvents, and, depending on the solute-solvent interactions thus induced, the $HgCl_2$ may suffer a complete loss of the triatomic linear molecular species (characteristic of the pure salt in its molten state) or, again, may dissolve molecularly. Other studies with such mixtures, and investigations of the Group II halides, in progress, are surveyed in this report.

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Contents

INTRODUCTION

Apart from the interest in molten inorganic salts from the viewpoint of a class of high temperature materials, work in this area has been stimulated by the need for knowledge fundamental to understanding the behavioral aspects of this class of liquids. It is generally recognized that certain inorganic salts, such as NaCl, consist predominantly of ions in the molten state. Such melts constitute a class of electrolytes that are truly "ionic liquids", in contrast to ambient temperature electrolytes which generally consist of a mixture of two components, the ionic "solute" and a molecular "solvent". A trend to more chemical problems in the past two years is also apparent in fused salt research. Mixtures of molten salts have been noted to behave, not infrequently, as if they contain "new" species in addition to the ionic components of the constituent salts.

It was recognized that a need exists, quite aside from the studies of fused salt mixtures, for knowledge of the behavioral aspects (structure, physical properties) of selected melts of pure one-component salts. A significant part of the effort of this research has been

directed to physical property measurements, as precisely as possible, for structural studies in this area. The most popular molten salts have been the alkali halides, specifically NaCl and KCl. A characteristic of these melts is that the cationic and anionic species are both spherical, with the external valence electronic shells the same as those of the rare gas elements (e.g. helium, argon). The attention in this program was directed to inorganic salts in which the liquid state interactions would be at least one degree more complex, e.g. salts containing spherical cations but planar anions (nitrates), and those with a very pronounced degree of covalent bonding for which "molecular" melts could be predicted (mercuric halides). Work has also been initiated in the Group II halides, for which the anionic species are the same as the alkali chlorides, and in which the effect of more complex electronic structures of the cationic species in the behavioral aspects of molten salts can be approached.

EXPERIMENTAL FEATURES

The design of physico-chemical techniques for precise property measurements in liquid state systems at elevated temperatures (200°-1000°C) has been a continuing work. In the present period, the techniques of high temperature viscometry have been developed as required for "ionic" and "molecular" salts. High temperature instrumentation for electrical conductance, density, surface tension, cryoscopy, phase-transition calorimetry, and Raman spectroscopy is available in this Laboratory, and has been used as required for the studies in progress.

DISCUSSION

Molten Nitrates: Next to alkali chlorides, the nitrates have probably been most widely studied. There are several reasons for this; the fact that the nitrates are low-melting salts, readily investigated using Pyrex glass apparatus has undoubtedly been a primary consideration. The failure of the theories used for the behavioral aspects of the alkali halides when applied to nitrates has been examined. A disc-shaped model of the nitrate ion, 2.3Å radius and 2.2Å thickness, has been advanced in the discussion of the properties and structure of molten nitrates. It appears reasonable that the nitrates, like the alkali chlorides, form highly ionized liquids on fusion, in which the ions are predominantly kinetically free. The lower values of the transport parameters (diffusion, electrical conductance) of molten nitrates may be attributed, in large part, to the lower kinetic energy of these systems.

A comparison of $AgNO_3$ and $NaNO_3$ as solvents for various ionic salts is in progress to evaluate ionic interactions. The techniques of Raman spectroscopy and the thermodynamic method of cryoscopy are used in these studies. An interest has been to investigate the possible interactions arising to asymmetry effects when divalent species, such as Ca^{++}, Mg^{++}, are dissolved in the above one-component melts as solvents. Interpretation of these results awaits work in progress. As part of this project, precise thermodynamic data, from heat of fusion calorimetry, for $AgNO_3$ and $NaNO_3$ have been gained.

<u>Molten Mercuric Halides</u>: The behavioral aspects of the one-component melts for pure $HgCl_2$, $HgBr_2$ and HgI_2 have been characterized by precise physical property measurements in this Laboratory. It is apparent that the mercuric halides form liquids on melting that are essentially molecular. These salts do ionize in the molten state, but the degree of ionization is quite small, e.g., $\alpha = 10^{-5}$, 10^{-4} and 10^{-2} for the melts of $HgCl_2$, $HgBr_2$, and HgI_2, respectively. The predominant species in the liquid state from these salts have been confirmed to be linear triatomic molecules.

Studies in which the interactions lead to new chemical species appear very promising in molten salt solvents that are essentially molecular rather than ionic. The salient results to date here show that with appropriate inorganic salts as "solvents", such molecular liquids can be readily dissolved. An interesting aspect here is that with the addition of the second component, interactions can be induced such that the mercuric halide melt retains its molecular identity or transforms almost entirely into ionic species. Solution of $HgCl_2$ in molten KCl is an example of the latter; at 70 mol% KCl, the mercuric chloride solute is found predominantly as $HgCl_4^{=}$. The change in ionicity of the Hg-Cl bonding from that in pure molten $HgCl_2$ to that as $HgCl_4^{=}$ has been assessed as part of this study. By contrast, the dissolution of $HgCl_2$ in molten $TlNO_3$ apparently leads to a liquid state mixture in which $HgCl_2$ retains its identity as tri-atomic linear molecular species (Raman spectra, cryoscopy). The preceding is an example of work currently in progress.

A series of cryoscopic studies of mixtures of molten salts, with the mercuric halides as solvents, and alkali halides as solutes have been part of this work. Final interpretation of these data awaits theoretical calculations in progress.

Molten Group II Halides: Relative to the alkaline earth halides, the molten salts form a class of ionic liquids in which the interactions are at least one degree more complex than in the pure molten alkali halides. The outstanding experimental data required to assess the physical properties and structural aspects of the molten Group II halide salts are viscosities and heats and entropies of fusion. Research samples of selected halides for Mg, Ba, Sr, and Ca have been prepared for this program. Heat of fusion measurements have been completed for $BaCl_2$ and $SrCl_2$. Measurements of viscosities required refinements of the high temperature techniques for such halide melts; the experimental effort in this phase of the work was guided accordingly to meet this objective, and measurements for the molten halides will be possible in the near future. Strontium chloride has been selected for first attention in order to assess the theoretical concepts of fused salt chemistry relative to the physical properties and structure of the Group II halides.

Technical Reports

1. Physical Properties and Structure of Molten Salts; AFOSR Report 446 Contract No. AF49(638)-978. (1961)

2. Molten Salt Bibliography; AFOSR Rpt. 786; Contract No. AF49(638)-978. (1961)

Research Papers

1. J. Chem. Ed. 39, 59 (1962): Physical Properties and Structure of Molten Salts (Janz)

2. Electrochimica Acta 7, 427 (1962); Molten Nitrates as Electrolytes (Janz et al.)

3. J. Electrochem. Soc. 109, 842 (1942); Molten Mercuric Halides as Electrolytes (Janz et al.)

Related Bibliography

1. J.Chem.Phys. 35, 739 (1961); Raman Spectra and Ionic Interactions in Molten Nitrates (Janz et al.)

2. J.Chem.Phys. (in Press)(1963); Vibrational Spectra of Molten Halides of Mercury, Part I., $HgCl_2$, $HgBr_2$ and HgBrCl (Janz et al.)

3. J.Chem.Phys. (in press) (1963); Vibrational Spectra of Molten Halides of Mercury, Part II., HgX_3^- and $HgX_4^=$ Ions (Janz et al.)

4. J.Electrochem. Soc. 108, 1052 (1961) Molten Carbonates as Electrolytes; Physical Properties and Mechanism of Conductance (Janz et al.)

5. J. Electrochem. Soc. (in press) (1963) Molten Carbonates as Electrolytes; Viscosity and Transport Properties (Janz et al.)